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by

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Spectrum-Line Reversal Measurements of Free Electron
and Coupled N_2 Vibrational Temperatures
in Expansion Flows

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Spectrum-line reversal measurements of the excitation temperature of Na atoms in expansion flows of shock-heated Ar and Ar + 1% N_2 mixtures are described. The measurements were made in a conical nozzle attached to the end of a conventional shock tube. For expansion flows of pure Ar from reservoir temperatures of 3200 to 4200°K and a reservoir pressure of about 37 atm, the measured Na temperatures ($\approx 2200^\circ\text{K}$) were considerably in excess of the local translational temperature ($\approx 400^\circ\text{K}$). These high excitation temperatures are interpreted in terms of the excitation of Na by free electrons produced from ionization of the Na in the reservoir. On this basis, free electron temperatures are deduced which indicate freezing of the electron thermal energy at values corresponding to those expected at the nozzle throat. This result suggests a slow rate of transfer of electron thermal energy to the Ar translational mode.

The addition of 1% N_2 to the Ar expansions produced large reductions in the measured Na temperatures. The

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reduced temperatures are shown to correspond to the frozen N_2 vibrational temperatures expected on the basis of previous results. These reductions are explained in terms of an efficient transfer of the excess electron thermal energy to the N_2 vibrational mode, the free electron and N_2 vibrational temperatures being thereby coupled and equilibrated during the expansion.

The present results also substantiate the faster vibrational relaxation rates inferred previously from similar expansion flow studies of pure N_2 ; they further suggest that the simple Landau-Teller rate equation, when used with relaxation times measured in shock wave flows, is not adequate to describe the vibrational relaxation process under the extreme nonequilibrium conditions associated with nozzle-expansion flows.

1. INTRODUCTION

Studies of flows at high temperatures have generated considerable theoretical discussion of thermal and chemical nonequilibrium processes under the extreme conditions associated with very rapid expansion flows. While it has been the practice in those discussions to extrapolate phenomenological descriptions of reaction processes and reaction-rate data obtained in other environments directly to the expansion flow situations, there has been little actual experimental confirmation to justify this current practice. The lack of experimental justification for such extrapolations prompted Hurle, Russo and Hall in an earlier paper to examine the validity of these extrapolations experimentally in relatively simple expansion-flow environments.

In Ref. 1, the authors report the experimental study of the behavior of N_2 vibrational relaxation in a supersonic nozzle-expansion flow. The results of that study showed that the apparent rate of vibrational relaxation during the expansion was faster than that observed behind shock waves. This result indicated that the simple Landau-Teller relaxation equation, when used in its present form with shock-tube measured relaxation rates, is not adequate to describe the vibrational relaxation process in the expansion-flow environment examined.

In view of those observations and their possible significance in relation to the vibrational relaxation process under other conditions of extreme non-equilibrium, it was stressed that an independent confirmation of the conclusions of Ref. 1 is clearly desirable. In the meantime, we have carried out additional studies in both shock-wave and expansion flows to further substantiate those conclusions. The shock-wave studies provided added confirmation of the ability of the Na-line reversal method (as used in Ref. 1) to measure N_2 vibrational temperatures and relaxation times; these studies have been reported elsewhere.² The expansion-flow studies, which further substantiated the above conclusions, also led to the observation of other interesting nonequilibrium phenomena; these observations are reported in the present paper.

In the present studies, Na-line reversal temperatures were initially measured in expansion flows similar to those used in Ref. 1, but in which Na excitation due to vibrationally excited molecules was absent. In the absence

of vibrationally excited molecules, or other species efficient in electronically exciting sodium atoms, the Na-line reversal temperature will be governed by the (inefficient) exchange of translational energy with Na electronic excitation. Thus, for Na in a monatomic heat bath, the reversal temperature would be expected to be near or somewhat lower than the temperature of the heat bath, depending on the relative efficiency of Na excitation by the monatomic gas and the efficiency of radiative depopulation of the excited Na state.

Accordingly, line-reversal measurements were carried out (using the techniques of Ref. 1) to verify the expected absence of sodium excitation in nozzle-expansion flows of argon, in which the argon temperature was very low. However, contrary to these expectations, the preliminary observations in the nozzle flows indicated strong Na emission, characteristic of a very high Na excitation temperature ($\approx 2500^\circ\text{K}$), although the argon heat bath was at a temperature of only a few hundred degrees.

This anomalous behavior prompted a detailed examination of Na-line reversal temperatures in Ar expansion flows. The present paper, in part, describes the results of these measurements made over the range of reservoir (reflected shock) temperatures from 3200° to 4200°K . The high reversal temperatures observed in these expansions are explained in terms of the efficient excitation of Na atoms by free electrons. The electrons are produced by ionization of the Na in the reservoir region where the electron concentration is relatively high because of the low ionization potential of Na (≈ 118 kcal/mole). This concentration may be expected to remain nearly constant during the expansion as a consequence of the vanishingly small three-body electron-ion recombination process. On this basis, it is shown that the measured Na temperatures in these expansions agree very well with free electron

temperatures frozen at the nozzle-throat values. Thus, since the electron temperature in the present expansions is determined essentially by the rate of thermalization of the electron energy with the Ar heat bath, the inferred free electron temperatures indicate a slow rate of equilibration of electron thermal energy with the translational mode of argon.

The observation of relatively high electron temperatures and concentrations in the Ar expansion flows raised an important question concerning the results of the earlier work. The same amounts of Na additive were used, under similar conditions of reservoir temperature and pressure, in the initial N_2 expansions¹ in which lower Na excitation temperatures were observed. In those expansions there is no question that even in the presence of these electrons the Na-line reversal temperature would monitor the N_2 vibrational temperature, since the amount of N_2 was of the order 10^6 times larger than the electron concentration. However, there was a question whether the electrons, through direct interaction with the N_2 vibrational degree of freedom, could have enhanced the rate of vibrational de-excitation and so produced the apparent faster vibrational relaxation. This question prompted a theoretical investigation³ of the efficiency of thermal energy transfer between free electrons and N_2 vibration. While this investigation showed that any effects of N_2 vibrational de-excitation by free electrons would be unimportant under the expansion conditions of Ref. 1, it further suggested that the free electron and N_2 vibrational temperatures would be closely coupled in such environments.

The experimental examination of an environment in which there exist two individual, but probably coupled, relaxation processes associated with the free electron and N_2 vibrational energies was an attractive proposition. Not only would the results of such an examination perhaps contribute towards an

understanding of coupled relaxation processes, but the experimental knowledge of a close coupling between free electron and molecular vibrational temperatures would also be of considerable practical importance in other nonequilibrium environments, such as in re-entry flows, where it could act to significantly reduce the free electron temperature. Accordingly, the present Na-line reversal measurements were extended to examine similar expansion flows containing 1% N_2 . The results of these studies are also reported in the present paper.

These dilute N_2 experiments were carried out over a range of reservoir conditions covering those used for the Ar expansions. The addition of the 1% N_2 was observed to greatly reduce the Na temperatures measured in those expansions. This effect is explained in the present paper in terms of the proposed³ efficient transfer of electron thermal energy to the N_2 vibrational mode. The process results in the rapid equilibration of the free electron and N_2 vibrational temperatures during the expansion, the N_2 vibrational temperature being effectively unchanged by this interaction process. In support of this interpretation, the measured Na temperatures are found to agree, over the entire range of reservoir temperatures from 2600° to 4200°K, with those expected for the N_2 vibrational temperature on the basis of the results of Ref. 1. The significance of this observation is discussed in the light of the results of the previous work and with respect to other nonequilibrium environments.

In the present paper, the experimental arrangement is briefly described in Sec. 2. The results for the 100% Ar expansions are described and discussed in Sec. 3 and the results for the dilute N_2 expansions are discussed in Sec. 4. The combined results are finally discussed more fully in Sec. 5.

2. EXPERIMENTAL METHOD

The shock-tube and nozzle apparatus used for the present experiments has been described in detail previously in Ref. 1. The shock tube is a conventional reflected-shock type in which helium was used as the driver gas. The test gas in the driven tube was initially separated from the convergent-divergent nozzle by a scribed copper diaphragm. This copper diaphragm bursts, without fragmenting, under the pressure developed behind the shock wave reflected from the nozzle entrance, thereby initiating the expansion flow in the nozzle. Steady flow conditions are established throughout the nozzle in about a hundred microseconds. The nozzle instrumentation and optical system used for line-reversal temperature measurements are described fully in Ref. 1.

In the present experiments, sodium excitation temperatures were measured in the nozzle at an area ratio of 8, which is about 3 inches from the nozzle throat (the area ratio is defined as the ratio of the local nozzle area to that at the nozzle throat). For the argon expansions, in which the Na temperatures were high, some measurements were also made at an area ratio of 32.

As in the previous work, the shock tube was evacuated to less than 0.2μ Hg prior to loading with test gas; the tube had an apparent rate of pressure rise of 1μ Hg/min. The nozzle assembly was evacuated to about 0.05μ Hg. The argon and nitrogen used in these studies were taken from standard cylinders with purity levels, specified by the manufacturer, of 99.998% and 99.996%, respectively, and were used without further processing. The argon-nitrogen mixtures were obtained by premixing argon and nitrogen in a stainless steel mixing vessel and stirring the mixture. For the range of initial

shock-tube pressures used in these experiments, namely 250 to 400 mm Hg, the maximum impurity content of the test gases and gas mixtures was 30 ppm. The sodium atoms were introduced into the shock tube in the form of trace amounts of NaCl smoke together with the test gas.

The experiments were carried out over a range of reservoir temperatures for reservoir pressures of about 37 atm. For the argon flows, reservoir temperatures in the range of 3200°K to 4200°K were used. For the 1% N₂ flows, the increase in the net rate of sodium excitation by the N₂ molecules permitted reversal temperature measurements for reservoir temperatures as low as 2600°K. The precise reservoir conditions for all runs were determined from simple shock-tube theory on the basis of the measured wave speed between several stations over the last half of the shock tube.

3. OBSERVATIONS FOR 100% ARGON EXPANSIONS

Measured Sodium Temperatures

Sodium excitation temperatures, T^* , observed at an area ratio of 8 during the expansion flows of 100% argon are shown in Fig. 1 for a range of reservoir temperatures, T_0 , from 3200 to 4200°K. The reservoir pressures, P_0 , were within ± 5 atm of a mean value of 37 atm for the six data points indicated. The lowest curve in this figure illustrates the local argon translational or heat bath temperature and corresponds to sodium excitation temperatures in thermal equilibrium with the argon bath. It is clear that the observed sodium excitation temperatures are considerably higher than the corresponding heat bath values, suggesting a highly energetic source of sodium excitation.

The Na excitation temperature is defined by the Boltzmann relation in terms of the ratio of the population of the excited (²P) to the ground (²S) elec-

tronic states. The population of the excited state is maintained by the balance between the collisional excitation processes and the combined collisional quenching and radiative emission processes. For exciting species having a Boltzmann distribution of energies the sodium excitation temperature can be related to the effective temperature of the energy mode which is associated with the excitation process. It is the determination of this source of excitation with which we now concern ourselves.

Source of Sodium Excitation

The greater part of the thermal energy of the expanded gases is contained in the translational degrees of freedom of the argon atoms. The conversion of random thermal energy to directed kinetic energy during the nozzle expansion results in a rapid fall of the Ar translational temperature. For example, at the area ratio of 8 this temperature has fallen to about 1/8th of the initial reservoir temperature, so that the local Ar temperature at the observation station lies between 300 and 500°K. Thus, any Na excitation corresponding to temperatures in excess of these values cannot be associated with neutral argon atoms. The low reservoir temperatures furthermore preclude any significant Na excitation due to metastable Ar which may be present in the expansion; the lowest metastable level has an excitation energy around 300 kcal/mole and the largest mole fraction of Ar species in this level is only about 10^{-16} in the reservoir at a temperature of 4200°K.

The high observed excitation temperatures of the Na must therefore be due to collisions with some species which, although present in very small amounts, exhibit a high degree of nonequilibrium in some particular energy mode as a result of the rapid expansion process. Further, this mode must be efficient in the transfer of energy to sodium atoms.

On the basis of the impurity levels, the only significant species apart from Ar present in the expansions are Na, Cl, Na^+ and electrons, the ions and electrons being formed in the high-temperature reservoir region. The amount of Na added to one mole of the shocked gas, as calculated³ from a comparison of the resonant emission of Na with that from known amounts of Cr in identical expansion flows,¹ is about 2×10^{-5} mole. The ionization of this amount of Na in the reservoir region at 4200°K produces an equilibrium electron mole fraction of about 10^{-5} . Since the total gas pressure falls from its initial value of about 37 atm in the reservoir to 0.2 atm at the observation station in about 100 μsec , any changes in the ion concentration due to three-body recombination during this rapid expansion would be expected to be small. The degree of ionization in the expansion can therefore be considered to be frozen approximately at its reservoir value. The estimated mole fraction of Na additive is probably accurate to within an order of magnitude for each experiment, so that the electron mole fraction calculated from Sahas' equation is, for frozen flow, reliable to within a factor of 3.

From classical elastic collision theory, the sodium and chlorine atoms and ions present in the expansion can be expected to have the same low kinetic temperature as the argon atoms. However, this may not be true for the electrons since the classical amount of energy transferred per elastic collision between these light species and the heavy Ar atoms is very small. Thus, in the very rapid expansion, the rate of transfer of electron thermal energy to the Ar translational mode may be sufficiently slow that the electron temperature lags behind the falling Ar temperature and, as the collision frequency is further reduced, subsequently freezes at a relatively high value. Further, the excitation cross section of electrons with sodium atoms is greater than that

for Na excitation by heavy particles, so that, although the electrons are present only in small concentrations, it appears that the observed high Na excitation temperatures in the Ar expansions are most likely to be associated with the temperature of the free electrons.

Free Electron Temperatures

Considering the Na excitation to occur by collision with electrons having a Boltzmann distribution of energy characterized by a temperature T_e , and the Na quenching to occur both by electrons and the dominant Ar species, it can be shown from considerations of detailed balancing that T_e and the Na excitation temperature, T^* , are related by

$$\exp(-E/RT^*) = \left(1 + Z_{Ar}/Z_e + 1/Z_e \tau\right)^{-1} \exp(-E/RT_e). \quad (1)$$

In this equation, Z_{Ar} and Z_e are the effective collision frequencies for the quenching of the Na (2P) state by Ar and by electrons; E is the excitation energy and τ is the radiative lifetime of this state; R is the molar gas constant. The collision frequencies are given by $Z_x = [x] \sigma_x (8\pi RT/\bar{m}_x)^{1/2}$, where $[x]$ is the concentration of Ar or electrons in particles/cm³ at the observation station, σ_x is the relevant quenching cross section, \bar{m}_x is the reduced mass of the colliding pairs and T is the kinetic temperature.

The particle concentrations are obtained from the known expansion ratio and the initial reservoir conditions; the electron concentrations are obtained from Sahas' equation. The cross section, σ_{Ar} , for the quenching of Na excitation by argon can be estimated from previous Na-line reversal temperatures measured behind incident shock waves in Ar,⁴ in which the measured temperatures were found to be about 200°K lower than the Ar kinetic temperature. Interpreting this result as due to radiative depopulation of the excited

Na, resulting from the inefficiency of Na excitation by Ar, yields a value $\sigma_{Ar} \approx 1 \times 10^{-17} \text{ cm}^2$.

The cross section, σ_e , for the quenching of Na excitation by electrons would be expected to be considerably larger than σ_{Ar} because electron quenching involves the charge-interaction of the optical electron in the sodium atom with the perturbing free electron. A value of $40 \times 10^{-16} \text{ cm}^2$ has been quoted⁵ for the electron excitation cross section from the early work of Christhof,⁶ while values of $90 \times 10^{-16} \text{ cm}^2$ and $170 \times 10^{-16} \text{ cm}^2$ are indicated respectively by the work of Allis and Morse⁷ and that of Brode,⁸ quoted in Ref. 9. Because of this uncertainty in σ_e , values of 50, 100 and $200 \times 10^{-16} \text{ cm}^2$ are used in the present calculations but it will be seen that the actual magnitude in this range is not essential to the interpretation of the results. The well-established value for the radiative lifetime, τ , is taken to be $1.6 \times 10^{-8} \text{ sec}$.¹⁰

On these bases, sodium excitation temperatures have been calculated for the range of experimental conditions used in the Ar expansions, and are shown in Fig. 1. The upper curve in this figure shows the Na temperature variation calculated from Eq. (1) for an electron temperature frozen at the reservoir value. The calculations are made for a constant reservoir pressure of 37 atm and a constant Na mole fraction of 2×10^{-5} , using the values $\sigma_{Ar} = 1 \times 10^{-17} \text{ cm}^2$ and $\sigma_e = 100 \times 10^{-16} \text{ cm}^2$. The Na temperature for electron temperatures frozen at $0.5 T_0$ and $0.75 T_0$ are also indicated. The effect of the four-fold variation in the value of σ_e is indicated for the $T_e = 0.75 T_0$ curve and it is noted that the dependence of T^* on this quantity is small. The effect of a similar variation in the argon quenching cross section is too small to be included.

It is noted from Fig. 1 that the calculated Na temperatures are very sensitive to the value used for the electron temperature. The temperatures calculated using the value $T_e = 0.75 T_o$, which correspond to the assumption that the electron energy distribution is frozen at the nozzle throat value, are in very good agreement with those observed. Early freezing of the electron energy during the expansion is consistent with the theoretical considerations in the preceding section.

Additional qualitative evidence for a frozen electron energy distribution in the flow was obtained by simultaneous measurements of the Na-line reversal temperature at a nozzle area ratio of 32, located 4 inches further down the nozzle. Strong Na emission observed at this station indicated high reversal temperatures but the reduced sensitivity, due to the lower gas density, did not permit an accurate quantitative analysis of this radiation data.

It is also noted that the electron concentration in the reservoir, calculated on the basis of the fixed amount of Na additive (0.002%), varied by an order of magnitude over the range of reservoir temperatures used in the above expansions. The agreement between observed and calculated Na temperatures for this range of variation of the electron concentration lends support to the interpretation that the electrons are the source of Na excitation. It is of interest to note that an increase or decrease in the concentration of the Na additive would not alter the correlation between the calculated curves and the experimental data. The effect would be to displace both the calculated curves and the experimental data together, either upward or downward, in Fig. 1 for increased or decreased sodium concentration respectively. This effect arises because the corresponding increase or decrease in the number density of electrons is reflected in the extent of the departure of the Na excitation temper-

ature from radiative equilibrium in Eq. (1) for both the calculated and observed Na temperatures

4. OBSERVATIONS FOR 1% N₂ + 99% AR EXPANSIONS

Measured Sodium Temperatures

Several of the argon expansions which were discussed in the previous section were repeated with the addition of 1% N₂. This addition of N₂ to the expansion flows was observed to result in striking reductions in the measured sodium excitation temperatures. Typical temperature data obtained from expansions with and without the addition of the 1% N₂ are listed in Table I, for similar reservoir conditions. It is noted from this table that a reduction in sodium temperature of about 700°K was observed for a reservoir temperature of 4200°K and a reduction of about 200°K was observed for a reservoir temperature of 3200°K.

Such large changes cannot be explained in terms of thermochemical effects attributable to the addition of N₂ to the argon flows. The maximum degree of N₂ dissociation (at 4200°K) is only 7×10^{-4} , which represents only 0.007% of the total Ar enthalpy. Further, N₂ does not appear to have a stable negative ionic state, so that the electron concentration in both the reservoir and expansion is expected to be the same as in the Ar expansions.

The N₂ does, however, provide a further source of Na excitation and quenching during the expansion process. The interchange of N₂-vibrational and Na-electronic energy is known to occur readily on collision, as was discussed in Ref. 1 and has been further illustrated recently in Ref. 2. Furthermore, the N₂ vibrational temperature in the present expansion is, on the basis of the results of Ref. 1, also expected to be frozen at a high value, though somewhat lower than the electron temperatures discussed above.

The lower observed Na excitation temperatures in the dilute N_2 expansions will thus most likely be associated with both the free electron and the N_2 vibrational temperatures. The actual measured Na temperature will depend not only on the relative efficiency of Na excitation by electrons and by vibrationally excited N_2 , but also on any coupling which may exist between the free electron energy and the N_2 vibrational mode.

Mechanism for Sodium Excitation

The addition of nitrogen molecules to the expansion flow necessitates that collisional terms be included in the expression for the sodium excitation temperature [Eq. (1)] to account for the interaction of the sodium electronic excitation with the nitrogen vibration. The more general form of Eq. (1) to account for the inclusion of these terms is

$$\exp(-E/RT^*) = \left(1 + Z_{Ar}/Z_e + Z_{N_2}/Z_e + 1/Z_e\gamma\right)^{-1} \left[\exp(-E/RT_e) + Z_{N_2}/Z_e \exp(-E/RT_v)\right] \quad (2)$$

In this expression, T_v is the N_2 vibrational temperature at the observation station and Z_{N_2} is the effective collisional quenching frequency of Na by N_2 . This frequency depends on the value of the Na- N_2 quenching cross section, σ_{N_2} . It is noted in Eq. (2) that in the absence of N_2 , the terms involving Z_{N_2} vanish and this equation reduces to Eq. (1).

A comparison of Eqs. (1) and (2) shows that, for similar expansion conditions, the value of T^* must change when N_2 is added to the Ar expansion. Provided that the value of T_e is not effected by the presence of the N_2 , the collisions of Na with vibrationally excited N_2 tend to elevate the value of T^* , as illustrated by the exponential term in the numerator of Eq. (2). In contrast, the added quenching of the excited Na by N_2 tends to lower this value, as

illustrated by the additional term in the denominator which is independent of the N_2 vibrational temperature.

It can be shown, as follows, that the quenching effect alone is not sufficient to account for the large reductions observed in the Na excitation temperatures. The maximum effect would occur when the N_2 vibrational temperature is in thermal equilibrium with the local Ar translational temperature. The rate of Na excitation due to N_2 vibration can then be neglected on the basis that $Z_{N_2} \exp(-E/RT_v) \ll Z_e \exp(-E/RT_e)$. Hence, Eq. (2) can be used to obtain the minimum value of Z_{N_2} and thus the smallest value of σ_{N_2} required to produce the observed reduction in T^* . The smallest value of σ_{N_2} is found to be $200 \times 10^{-16} \text{ cm}^2$ for the lowest reservoir temperature (3200°K) expansion and $1000 \times 10^{-16} \text{ cm}^2$ for the highest (4200°K). In addition to this unexpectedly large temperature dependence, these quenching cross sections are almost two orders of magnitude larger than the temperature-independent value of about $10 \times 10^{-16} \text{ cm}^2$ measured both in recent high-temperature shock-tube studies² and in low-temperature quenching experiments.¹¹

It is thus impossible to explain the observed lower Na temperatures on the assumption that the free electron temperature is unchanged in the presence of N_2 .

The observed low temperature may, however, be satisfactorily explained on the other hand in terms of a transfer of energy between thermal electrons and molecular vibration. In a recent paper,³ it is reasoned that free electron and N_2 vibrational temperatures are likely to be coupled in environments similar to the expansion flows described here. The calculations of Ref. 3, which are based on measurements^{12, 13} of the cross section for the excitation

of N_2 vibration by slow mono-energetic electrons, show that the transition probabilities for the thermal de-excitation of N_2 vibration by free electrons are several orders of magnitude greater than those for de-excitation by N_2 molecules. The thermal probabilities are also larger than the combined probability for the direct collisional transfer of electron thermal energy to both the N_2 translational and rotational modes. In view of these results, it was concluded in Ref. 3 that the thermal energy of free electrons in nonequilibrium expansions of N_2 will be transferred preferentially to N_2 vibrational energy. Because of this, it was further concluded that the free electron and N_2 vibrational temperatures will be rapidly equilibrated during the early stages of such expansions.

Although the above conclusions were made for expansions of 100% N_2 , it can be shown, as follows, that these conclusions are also likely to be true for the present expansions containing only 1% N_2 . Thus, following the analysis of Sec. 4 of Ref. 3 and using the transition probabilities evaluated in that reference, the time for the relaxation of the free electron temperature to the N_2 vibrational temperature is about 6×10^{-9} sec in the region of the nozzle throat and about 2×10^{-5} sec at the area ratio of 8, for the present expansion conditions with 1% N_2 . Since the expanding gas takes about 10^{-4} sec to travel between these locations, the free electron temperature will be expected to equilibrate with the N_2 vibrational temperature before the area ratio of 8 is reached. The transfer of the electron thermal energy will not significantly alter the N_2 vibrational temperature, since the amount of energy transferred is relatively small. For example, for an electron temperature frozen at 3150°K (where $T_e = 0.75 T_0$) the total electron thermal energy for one mole of test gas under the present expansion conditions is about 0.2 cal for a reservoir

temperature of 4200°K, while the vibrational energy of the 1% N₂ for a frozen vibrational temperature of 2000°K represents about 15 cal.

The equilibration of the free electron temperature with the N₂ vibrational temperature will thus not be expected to influence either the vibrational temperature or the vibrational relaxation process in the expansion.¹⁴ The vibrational temperature will thus be expected to be the same as in the absence of electrons. The Na excitation temperature will then be given by a modified form of Eq. (2) in which $T_e \equiv T_v$, so that

$$\exp(-E/RT^*) = \left(1 + Z_{Ar}/Z_e + Z_{N_2}/Z_e + 1/Z_e\gamma\right)^{-1} \left(1 + Z_{N_2}/Z_e\right) \exp(-E/RT_v). \quad (3)$$

In using this expression, the free electron temperature is considered to be both coupled to, as well as equal to, the vibrational temperature. The theoretical vibrational temperatures for the 1% N₂ + 99% Ar mixtures were calculated as shown below.

Interpretation of Measured Sodium Temperatures

The values of the N₂ vibrational temperature inferred from Eq. (3), using the observed Na excitation temperatures listed for the dilute N₂ expansions in Table I, are plotted in Fig. 2. The upper curve in this figure represents the theoretical N₂ vibrational temperatures calculated as in Ref. 1, from the Landau-Teller relaxation equation using a finite difference method.¹⁵

These theoretical temperatures were calculated on the basis that the Ar can be replaced, for relaxation purposes, by an equivalent effective amount of N₂. Recent work by Millikan¹⁶ has shown that the efficiency of vibrational de-excitation is inversely proportional to the square root of the mass of the colliding de-exciting species. Thus, for relaxation purposes, 1 atm of Ar can be considered to be equivalent to 0.84 atm of N₂, so that the effective

reservoir pressure for the total pressure of these experiments (37 atm) was equivalent to 32.7 atm of pure N_2 .

Using this scheme, the calculations were made using values of the local vibrational relaxation times appropriate to N_2 - N_2 collisions. These values are taken to be 15 times shorter than the corresponding times inferred from relaxation measurements^{2, 17} made behind shock waves. This factor is introduced in view of the results obtained in the previous expansions¹ of 100% N_2 which showed that, in expansion flows of the present type, the relaxation process as described by the Landau-Teller theory is characterized by apparent relaxation rates which are 15 times greater. It can be seen in Fig. 2, that the results of these calculations are in very good agreement with the experimental results.

The lower curve, which represents the translational temperature of the expanded gas at an area ratio of 8, is included in this figure to illustrate the extent of the departure of nitrogen vibration from equilibrium.

Coupled Free Electron- N_2 Vibrational Temperatures

The agreement between the inferred and calculated N_2 vibrational temperatures strongly supports the conclusion that the reduction in the Na temperature observed when 1% N_2 is added to the Ar is due to the equilibration of the free electron temperature with the N_2 vibrational temperature. On this basis a combined plot of the frozen free electron temperatures inferred from the measurements in the present experiments is shown in Fig. 3. The upper curve in this figure represents the free electron temperatures frozen at the nozzle throat in the Ar expansions in the absence of N_2 additive. The lower curve shows the free electron temperatures, which correspond to the frozen N_2 vibrational temperature, for the addition of 1% N_2 to the Ar expansions.

The reductions in the free electron temperature are seen to be over 1000°K at the high reservoir temperatures, corresponding to a reduction of over 30%. At the low reservoir temperatures, the reduction is about 20% (400°K).

5. DISCUSSION

Frozen Electron Temperatures

The result that the free electron temperatures are frozen in the present Ar expansion flows implies that the thermalization of the electron energy with the argon atoms is, under the present experimental conditions, a relatively slow process. This result has been anticipated before (see, for example, Sherman and Talbot,¹⁸ Grewal and Talbot,¹⁹ and Bray²⁰), but a quantitative measure of the extent of this type of nonequilibrium has apparently not been obtained previously under simple expansion conditions which are relatively free from the complexity of recombination processes.

Thus, while the experimental work and discussion of Refs. 18 and 19 can be said to indicate the existence of high electron temperatures in expansion flows of ionized Ar from a plasma source, these temperatures are mainly due to the ion-recombination process in which electrons are the stabilizing third bodies, rather than to the slowness of electron thermalization with the argon atoms. The high electronic excitation temperatures of Ar observed in the plasma-jet studies of Adcock and Plumtree²¹ may, perhaps, also be indicative of nonequilibrium electron temperatures arising in that way. However, we point out that the authors in Ref. 21 do not interpret their results as indicative of nonequilibrium electron temperatures, but rather of the attainment of local thermodynamic equilibrium between the electronic excitation and the Ar translational modes at their nozzle exit.

While Bray²⁰ proposes that there will be no sudden freezing of the electron temperature in expansion flows in which Ar ions and electrons are recombining, the electron temperature in his analysis is considered to be determined mainly by the ion-recombination rate, rather than by electron thermalization. In the present expansion flows the Ar is not ionized and the sodium ion recombination is relatively insignificant, because of the very low initial ion concentrations.

Consistent with the remarks in the introductory paragraphs of the present paper, we note that Bray assumes the applicability of Petschek and Byron's²² mechanism for shock-wave ionization to expansion flow environments. This three-body recombination mechanism involves an electron as the third body, with the recombination energy shared between this electron and the formation of an electronically excited argon atom. The over-all recombination rate is thus governed primarily by the rate of decay of these excited species. In the experiments of Ref. 22 this decay occurs for the most part by quenching collisions with other electrons. In the low-pressure expansions considered by Bray ($P_0 \approx 0.5$ atm), the electron densities are very low and the radiative de-excitation processes will probably become relatively more important; the presence of considerable amounts of Ar emission is evident in the experimental studies of Refs. 18 and 21. It is noted in these respects that the emission processes would be likely to act to give a smaller steady-state concentration of excited Ar and so modify the form of the expression which Bray uses for the recombination rate.

N_2 Vibrational Temperatures

The interesting feature of the N_2 vibrational temperatures inferred from the dilute N_2 expansion is that they are characteristic of a relaxation process

which, as in the earlier¹ 100% N_2 expansions, is also about 15 times faster than that inferred behind shock waves. Several possible reasons were discussed and advanced for this result in the earlier paper,¹ but none could be identified conclusively. However, the present results now enable more definitive conclusions to be made.

The agreement between the relaxation rates inferred from the previous pure N_2 studies and the present dilute N_2 expansions supports our belief that impurities are not responsible for the observed apparent rapid vibrational de-excitation. It would be extremely unlikely that the different gases used had precisely the same degree of active impurity content. Furthermore, as pointed out earlier,¹ large molecules which are most efficient in de-exciting vibrational modes are more likely to be dissociated behind the reflected shock, prior to the expansion, and are thus not likely to be as important as in shock-wave flows.

The agreement between the results of the present and previous N_2 studies also makes it very unlikely that the faster relaxation is associated with atom-exchange processes of the type proposed by Bauer and Tsang.²³ The nitrogen atom concentration in the earlier N_2 expansions was exceeding small¹ and in the present dilute 1% N_2 expansions it is even smaller. Thus, in addition to the other reasons advanced in this respect in Ref. 1, an explanation by means of these exchange processes is even more unlikely.

The dominant collision partner for N_2 vibrational de-excitation in the earlier work was the nitrogen molecule. In the present work it is the argon atom. It thus appears that each de-excitation process, when interpreted using the Landau-Teller relaxation equation, gives rise to an inferred relaxation rate which differs from that obtained behind shock-wave flows. A peculiarity

in the behavior of N_2 - N_2 de-exciting collisions under nonequilibrium expansion conditions would not generally be expected to have an exact counterpart in Ar- N_2 de-exciting collisions; it is more likely that the peculiarity is in the behavior of the vibrationally excited N_2 molecule alone. This peculiarity could, as suggested earlier,¹ be associated with the possibility that de-excitation can proceed more efficiently than supposed via the upper vibrational levels. Such a behavior would require the introduction of an additional dependence on the vibrational temperature into the simple Landau-Teller relaxation relation.

However, whatever the reason for the faster relaxation process, the present results confirm that the Landau-Teller relation, when used in its present form together with shock-tube measured relaxation rates, is not adequate to describe the relaxation process under the conditions of large departure from thermal equilibrium existing in expansion-flow environments. Thus, we feel that theoretical predictions of the extent of vibrational nonequilibrium in nozzle flows, which are based on the present Landau-Teller assumptions, should be regarded with some reservation until these differences are explained.

Coupling of Electron and Vibrational Temperatures

The large reduction in the Na temperatures observed when a small amount of N_2 is added to the Ar expansion flows has been shown to be in accordance with the equilibration of the free electron and N_2 vibrational temperatures. Coupling between these energy modes can have significant consequences in a variety of expansion flows involving nonequilibrium, as discussed below.

The behavior of nonequilibrium processes in expansion flows has attracted a great deal of theoretical attention and necessitated many detailed analyses pertaining to flows of considerable thermal and chemical complexity. Many assumptions have been made in these detailed analyses on the basis of

relatively little direct experimental information. Such analyses must consider the simultaneous behavior and the interaction of many chemical processes and reaction mechanisms. The importance of coupled processes in such situations has been exemplified by Treanor and Marrone,^{24, 25} who consider the effect of a coupling between molecular vibration and dissociation; a survey of other nonequilibrium problems associated with airflows has recently been given by Cheng.²⁶

The results of the present study suggest that, in expansion flows of high-temperature air, the free electron and N_2 vibrational temperatures will be coupled. If a similar coupling were to exist between the free electron and O_2 vibrational temperature, as appears to be likely from the experimental results of Schultz and Dowell,²⁷ then the O_2 and N_2 vibrational temperatures could be equilibrated through energy transfer with free electrons. In view of the faster relaxation rates for O_2 as compared with N_2 , this equilibration could lead to an over-all reduction in the extent of vibrational nonequilibrium in the expansion. This would have two important effects. First, the electron temperature would be reduced, enhancing the rate of ion recombination. Second, the majority of atom recombinations may be expected to take place into the upper vibrational levels of the molecule formed, so that a more rapid rate of vibrational de-excitation could increase the rate of atom recombination.

CONCLUDING REMARKS

The line-reversal measurements of the sodium excitation temperature in expansion flows of Ar, dilute N_2 and pure N_2 ¹ have all been explained by means of simple excitation mechanisms; expressions have been derived which relate the measured Na temperatures to the free electron and vibrational temperatures of the expanding gas. For the Ar flows, the electron

temperatures were found to be frozen at high values. For the dilute nitrogen flows, evidence has been found that the free electron and N_2 vibrational temperatures are coupled in a single relaxation process. It is noted that, although the line reversal technique does not measure the free electron or the vibrational temperature directly, there is ample justification for relating these temperatures to the measured excitation temperatures.

In the 100% Ar expansions, the good agreement between theory and experiment over the wide temperature range strongly supports the interpretation of the Na excitation in terms of interaction with free electrons. This interpretation does not require a precise knowledge of the details of the electron-Na excitation process. It does, however, require that the electron energy distribution conform to a Boltzmann one. In the present Ar and dilute N_2 expansions, a Boltzmann distribution is virtually assured under the conditions of thermal equilibrium and high collision frequency in the reservoir region. The maintenance of a Boltzmann distribution in the free electron and N_2 vibrational energies during the present nozzle expansion is not so readily assured. However, for the former, we note that Andersen and Shuler,²⁸ in a recent consideration of the relaxation of a spatially isotropic two-species gas, do show analytically that an initial Maxwell (-Boltzmann) distribution of energy relaxes to the final equilibrium through a continuous sequence of Maxwell distributions. Similarly, analyses by Montroll and Shuler²⁹ and Osipov³⁰ convincingly justify the assumption that the vibrational energy distribution will remain Boltzmannian during the expansion. Further, the identical line-reversal temperatures obtained using Cr as well as Na in Ref. 1 provide experimental verification of the preservation of a Boltzmann distribution in vibration throughout the expansions considered here.

Finally, the present results indicate that, by using a simple experimental system and measuring technique, it is possible to examine not only single relaxation processes but also processes which are likely to be coupled in expansion flow environments.

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via the N_2 translational and rotational modes - by which the free
electrons may tend to equilibrate with the Ar translational temperature,
this mechanism will (using the results of Ref. 3) only increase the
overall rate of this equilibration process by 8% and this is not sufficient
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Table I

A comparison between the Na-line reversal temperature, T^* , observed in expansions of Ar, with and without 1% N_2 , from conditions of similar reservoir temperatures, T_o , and pressures, P_o

100% Ar			1% N_2 + 99% Ar		
T_o °K	P_o atm	T^* °K	T_o °K	P_o atm	T^* °K
4150	32	2640	4160	32	1920
3860	35	2400	3760	35	1740
3840	35	2350	3750	36	1750
3500	38	1990	3710	40	1700
3480	38	1960	3270	39	1600
3250	42	1780	3180	42	1570
- - -	-	- - -	2760	46	1440
- - -	-	- - -	2650	41	1410

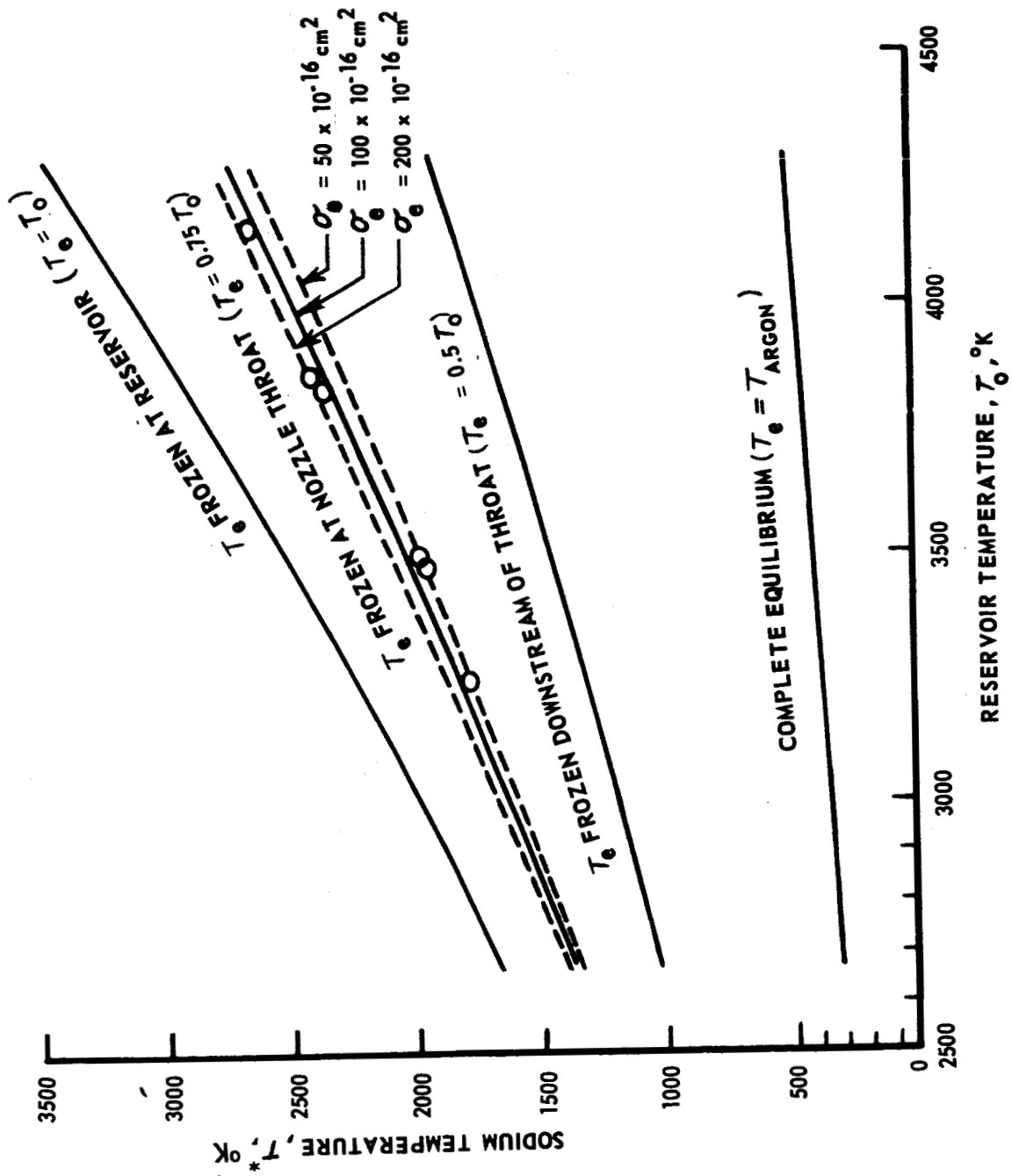


Figure 1

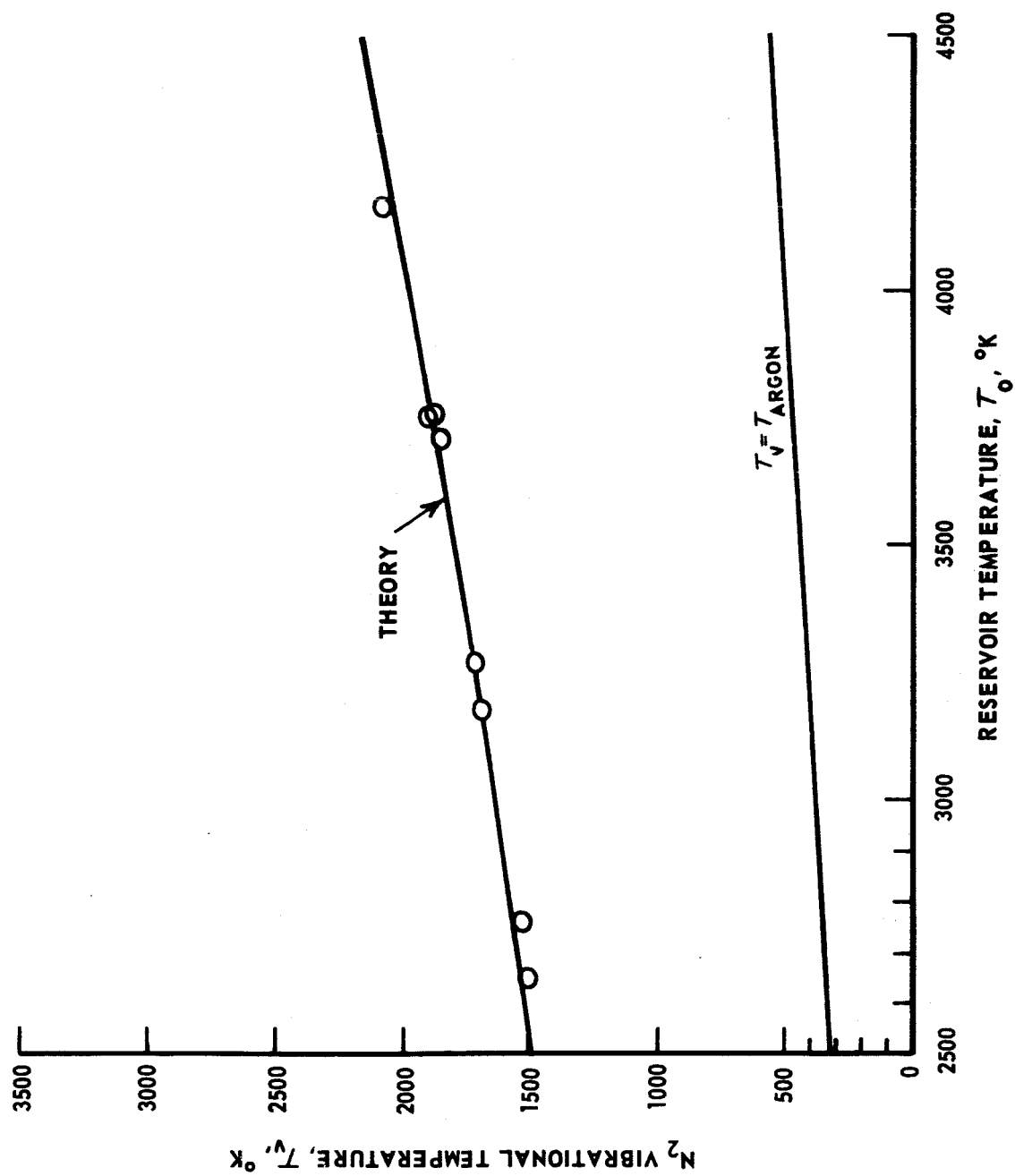


Figure 2

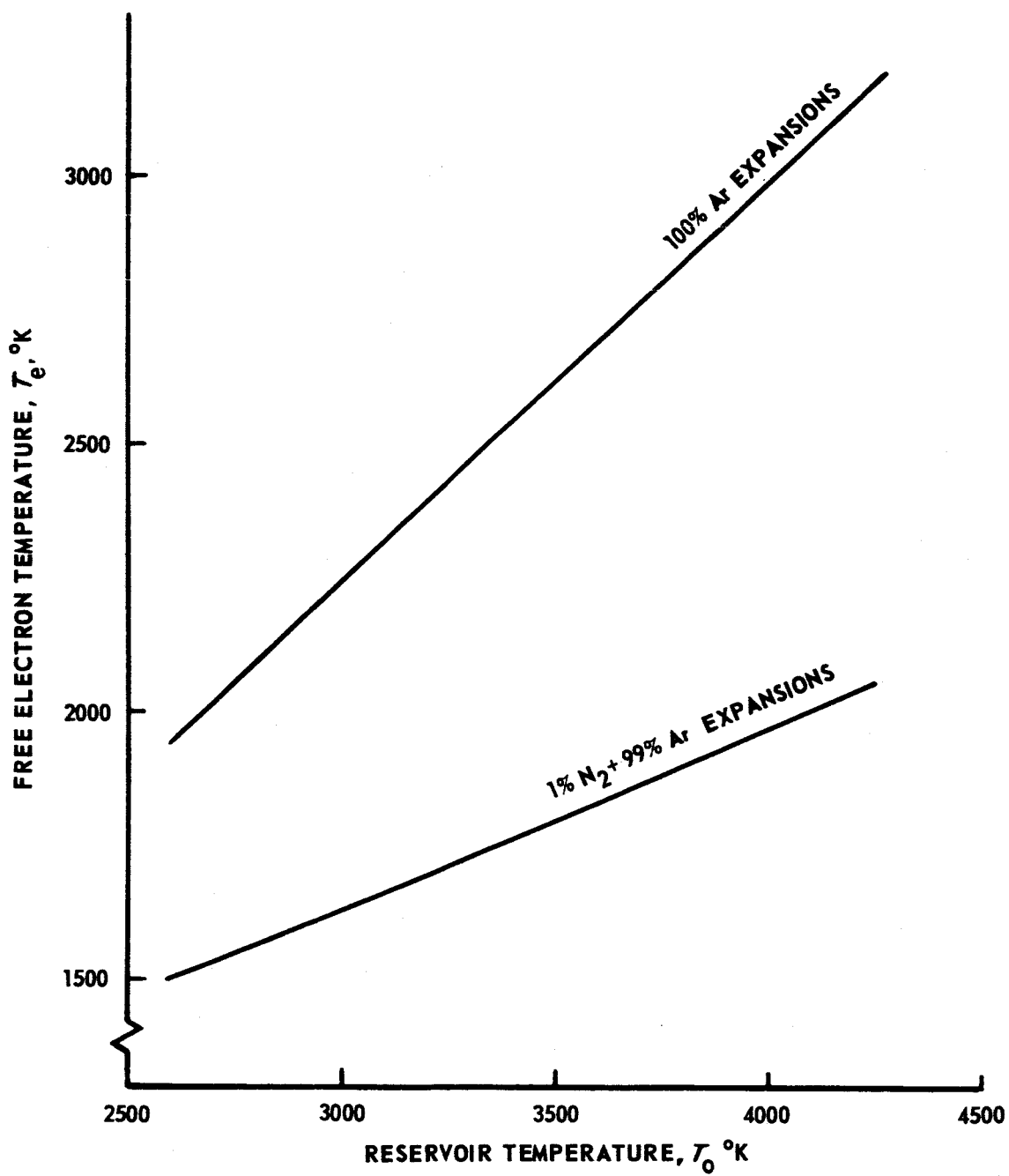


Figure 3

FIGURE CAPTIONS

- Figure 1 Comparison of Na excitation temperatures measured in the expansions of Ar + 0.002% Na with those calculated from Eq. (1) for free electron temperatures, T_e , frozen at various stages in the expansion. The hyphenated curves for $T_e = 0.75 T_o$ indicate the small dependence of the calculated Na temperature on the cross section, σ_e , for the excitation of Na by electrons.
- Figure 2 Nitrogen vibrational temperatures obtained from Eq. (2) using the Na temperatures measured in the expansions of 1% N_2 + 99% Ar, listed in Table I. The upper curve represents the theoretical N_2 vibrational temperatures, calculated for the faster vibrational relaxation observed in Ref. 1. The lower curve represents the vibrational temperatures for complete equilibrium during the expansion flow.
- Figure 3 Curves indicating the true reduction in the frozen free electron temperatures which results from the addition of 1% N_2 to the Ar expansion flows. These curves are obtained from Eqs. (1) and (2), using the measured Na temperatures and expansion conditions listed in Table I. The upper curve corresponds to electron temperatures frozen at the nozzle throat values, the lower curve to the equilibrated free electron and N_2 vibrational temperatures.